PHOTOMASK

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Adhesion control between resist patterns and photomask blank surfaces

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ABSTRACT

Most problems in photomask fabrication such as pattern collapse, haze, and cleaning damage are related to the behavior of surfaces and interfaces of resists, opaque layers, and quartz substrates. Therefore, it is important to control the corresponding surface and interface energies in photomask fabrication processes. In particular, adhesion analysis in microscopic regions is strongly desirable to optimize material and process designs in photomask fabrication. We applied the direct peeling (DP) method with a scanning probe microscope (SPM) tip and measured the adhesion of resist patterns on Cr and quartz surfaces for photomask process optimization. We measured adhesion and frictional forces between the resulting collapsed resist pillar and the Cr or the quartz surface before and after the sliding. We also studied the effect of surface property of the Cr and quartz surfaces to resist adhesion. The

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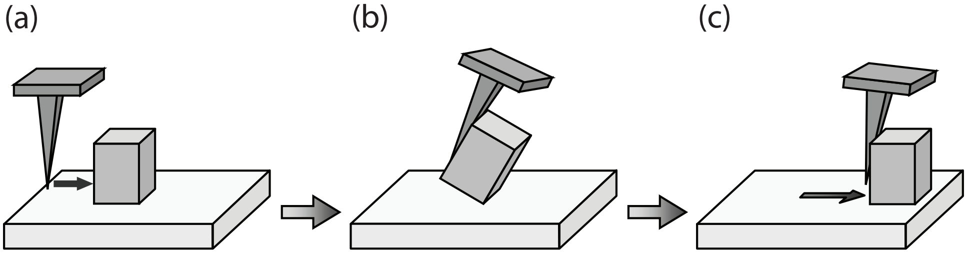

Figure 1. Schematic representation of a resist peeling process for adhesion measurements with SPM (a) scanning toward the resist pattern, (b) peeling off the resist pattern, and (c) sliding the resist pattern.

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EDITORIAL

The changing landscape for many photomask equipment suppliers

John Whittey, KLA-Tencor Corporation

What seems obvious to some may not be quite so clear for others, depending on the situation. I think most of us are well aware of the changing conditions of our industry as it has been touched upon with papers and editorials in the past. I am going to describe specifically the current situation with regards to market demand for certain types of photomask equipment in an effort to highlight what some equipment suppliers face in today's (and likely the mid to longer term) photomask making environment.

Due to rising costs and smaller unit volumes for leading edge masks the industry has decreased and consolidated for the last ten to fifteen years. The current model for merchant shops is to have one or possibly two leading edge R&D facilities worldwide. Since there are only four merchant companies left in the world that do leading edge work this means the amount of leading edge merchant manufacturing facilities is four or five. If we consider the addition of the captive shops then we can add in two to three in Asia, one in Europe (I am being generous here), and three in the United States. This brings us to a total of (on a positive side) twelve opportunities for sales for a given generation (node), and this is assuming that photomask makers purchase at least one of each new tool needed for a given node. Unfortunately, in reality, this is not the case as some photomask manufacturers skip a node or two depending on extendibility of existing equipment or budget constraints. This can mean that if single tool purchases are to take place for a given generation then the total market for an equipment generation is approximately eight to ten systems over about a thirty month period. With a market of eight to ten systems for a given tool generation it might not be out of the question to assume there are some risks involved for equipment manufacturers on obtaining an adequate return on investment.

What type of tools fall into this risk category? For a given generation or node I think e-beam lithography tools qualify, but perhaps with three or four more units for total market size (multiple tool purchases by one customer). Metrology tool customers such as critical dimension SEMs, pattern placement tools, and aerial imaging qualify. On the process side there are etchers, developers, repair, and cleaning systems that also fit the category.

Okay, so who cares if there is a paradigm shift and why is this important to photomask makers and their customers? On a long term basis in order for markets to be served there has to an adequate return on investment for a given amount of risk, otherwise markets will cease to be addressed. I believe this falls under the category of basic economic principles. This condition applies to photomask makers as well as their equipment suppliers. The question perhaps should be, "Not how much leading edge equipment or photomask sets cost?", but rather "Is the price being paid high enough to sustain long term economic viability of the market?" Semiconductor manufacturers ultimately have to bear responsibility for creating a sustainable model for this element of their manufacturing processes, but given current economic conditions I often wonder, "Who is looking out for the semiconductor manufacturers?"

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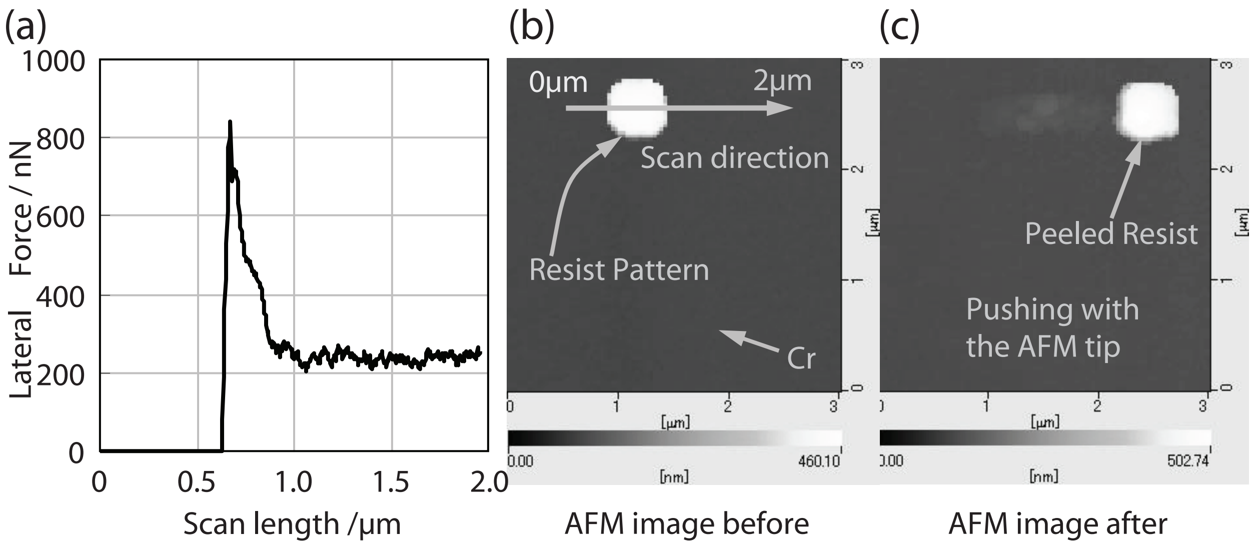

Figure 2. (a) An example of a lateral force - scan length curve measured during scratching the resist pattern. AFM images in tapping mode (b) before and (c) after the resist pattern.

adhesion could be controlled by surface modification using silanes and surface roughness on Cr blanks. We also discuss the relationship between the adhesion observed with the DP method and the properties of the modified surfaces including water contact angles and local adhesive forces measured from force-distance curves with an SPM.

1. Introduction

Recent problems in photomask fabrication such as pattern collapse, haze, and cleaning damage are related to the behavior of the surfaces and interfaces of quartz substrates, opaque layers, and resists. Therefore, it is important to control the corresponding surface and interface energies in photomask fabrication processes such as resist coating, patterning, resist stripping, and mask cleaning. For example, patterning is the most critical process in next generation photomask fabrication, because the probability of pattern collapse in this process increases as feature size decreases.

Adhesion analysis in microscopic regions during the patterning process is strongly desirable to optimize material and process designs in photomask fabrication. Scanning probe microscopy (SPM) has been used to characterize the adhesion property in lithographic processes used in semiconductor fields.[1,2] Figure 1(b) shows a schematic representation of a resist peeling process used for adhesion measurements with SPM, in which the resist pattern is collapsed by scratching the sample surface with an SPM tip. The adhesion between the resist pattern and the substrate is estimated from the maximum lateral force loaded to the cantilever when the resist pattern is collapsed. By adopting this direct peeling (DP) method, adhesion and peeling behavior of resist patterns on substrates can be quantitatively analyzed at the nanometer scale.

In this paper, we applied the DP method to adhesion measurement of resist patterns on Cr and quartz surfaces for the first time in the photomask industry in order to optimize the photomask fabrication process. We studied the optimized measuring conditions for the DP method. We also studied the effect of using silanization reagents to modify the Cr and quartz surfaces and surface roughness on Cr blanks on the adhesion measured with the DP method in order to promote resist adhesion.

2. Experimental Conditions

2.1 Adhesion measurement with the DP method and frictional force measurements

Photomask blanks comprising a Cr layer on a quartz substrate were used. Resist pillar patterns of various widths were fabricated on a Cr or a quartz surface by e-beam lithography. Positive-tone and negative-tone chemically amplified ebeam resists, abbreviated to p-CAR and n-CAR, respectively, were used for pattern collapse evaluation. These resists were based on polyvinyl phenol resin.

The principle of adhesion measurements with the DP method is explained in Fig. 1(b). The resist patterns were peeled from the Cr or quartz surface by an SPM tip. Figure 2(a) shows a lateral force - scan length curve measured during both the scratching shown in Fig. 1(b) and the subsequent sliding shown in Fig. 1(c). The tip was scanned toward a resist pattern at a constant height as shown in Fig. 1(a). The lateral force increased steeply after the tip came into contact with the resist pattern. A clear peak was observed and the force subsequently decreased and finally reached a constant level as the tip pushed the resist pattern.

Figures 2(b) and 2(c) show tapping-mode atomic force microscopy (AFM) images before and after the resist collapse, respectively. These images clearly show that the resist pattern was pushed by the tip after the collapse. The peak force in

Fig. 2(a) corresponds to the maximum lateral force required for the resist pattern to collapse. After the start of the collapse, the lateral force decreases gradually with the decrease in the area in chemical contact (i.e., the bonding area) between the bottom face of the resist pattern and a substrate surface. After the complete detachment of the chemical bonds, the resist pattern starts to be slid along the substrate surface by

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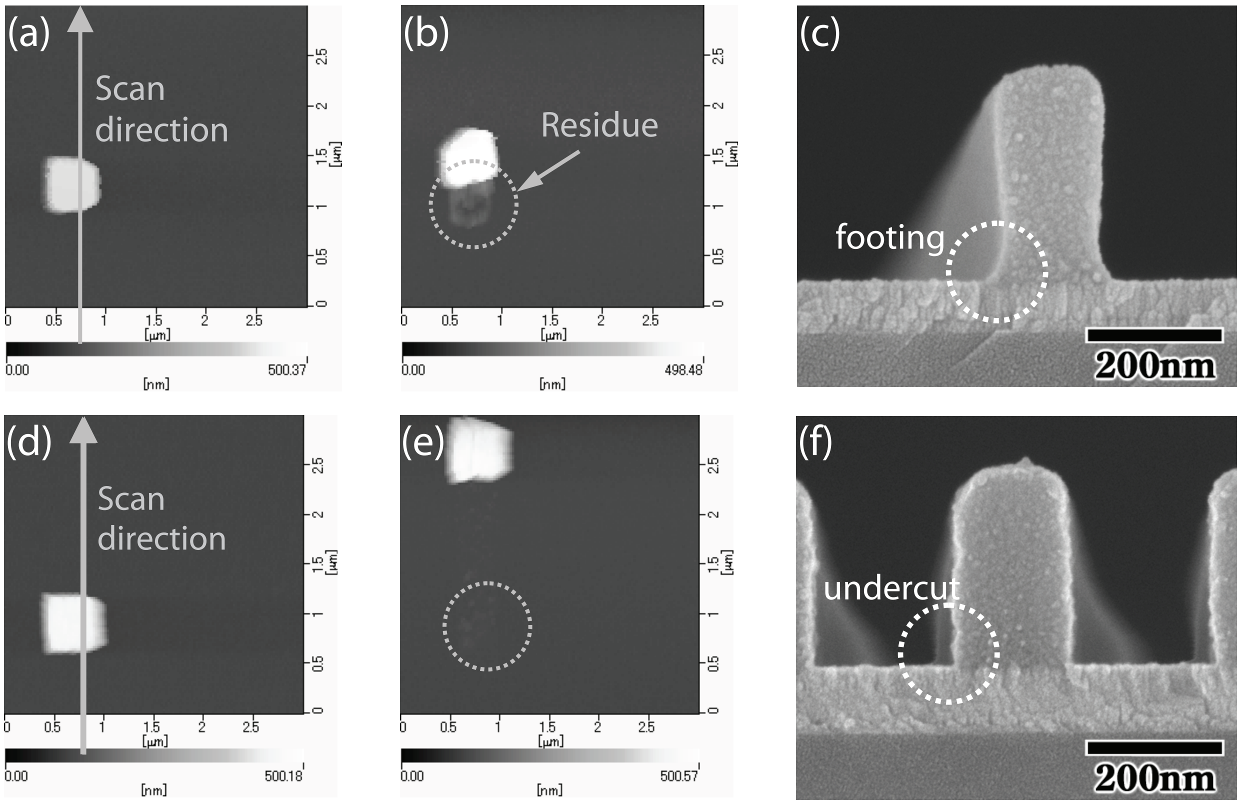

Figure 3. Resist type dependence for resist collapse behavior; AFM images of a resist pillar pattern on a Cr substrate (a) before and (b) after the scan under constant height mode. (c) A Cross-sectional SEM image for p-CAR. AFM images a resist pillar pattern on a Cr substrate (d) before and (e) after the scan under constant height mode for n-CAR. (f) A Cross-sectional SEM image of n-CAR.

the SPM tip, presumably after physical contact between the bottom face of the resist pattern and the substrate surface. This constant force during the sliding corresponds to a kinetic frictional force between the resist pattern and the substrate. The maximum and the constant lateral forces were measured as a function of the geometrical area of the bottom of the resist pattern (patterned area).

2.2 Sample preparation and characterization

Three types of commercially available Cr blanks were prepared in order to study the effect of surface roughness, the ebeam resist was patterned on these Cr blanks. Then, the adhesion was measured with the DP method. In order to change the surface energy of photomask blanks, their surfaces were chemically modified with silanization reagents, i.e., hexamethyldisilazane (HMDS) and octadecyltrimethoxysilane (ODS). These commercially available silanization reagents were used without further purification. Both Cr and quartz surfaces were processed by sulfuric acid/peroxide mixtures in order to obtain hydrophilic cleaned surfaces. Silanization was performed on both surfaces by the gas-phase chemisorption process. The e-beam resist was coated on the silanized substrates as well as on the cleaned Cr and quartz surfaces. After e-beam exposure and development, resist patterns were formed. The adhesion was measured by the DP method. The contact angles of water droplets on the modified and cleaned surfaces were measured with Drop Master (Kyowa Interface Science). The resist peeling test and surface roughness measurement were performed using a commercially available SPM (SII-NT L-trace). All measurements were performed under ambient conditions.

3. Results and Discussion

3.1 Lateral-force measurements for resist pattern collapse

First, we examined whether n or p-CAR was appropriate for the adhesion measurements with the DP method. Tappingmode AFM images of resist pillar patterns on a Cr surface before and after scanning with the DP method are shown for p-CAR, Figs. 3(a) and 3(b), and n-CAR, Figs. 3(d) and 3(e), respectively. Some residue from the p-CAR pattern remained on the Cr surface after the scan, while the n-CAR pattern was peeled from the surface and no residue was observed. To clarify the reason for this difference, we observed profiles of each resist pattern by SEM. As shown in Figs. 3(c) and 3(f), p-CAR and n-CAR exhibited footing and a slight undercut, respectively, at the interface between the resist and the Cr layer. In the case of p-CAR, the residue formation after pattern collapse can be explained in terms of the concentration of stress in the vicinity of the bottom part of the resist pattern.[3] From the observation described above, the n-CAR resist pattern was used for collapse experiments with the DP method in the remainder of this work.

Figures 4(a) and 4(b) show the dependence of the maximum lateral force for the resist pattern collapse and the kinetic frictional force for resist sliding on the size of the patterned area

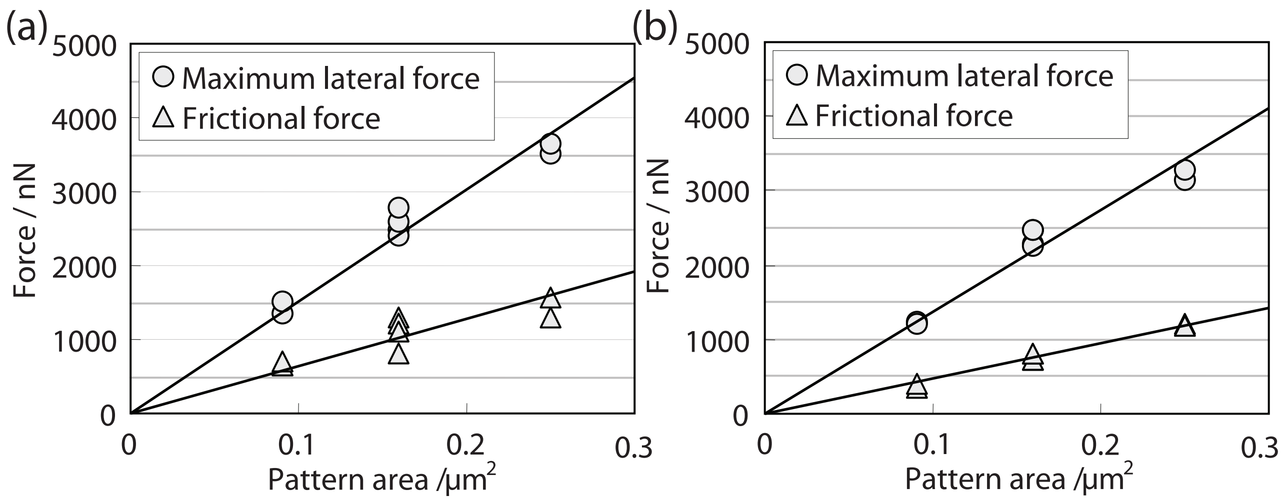

Figure 4. Dependence of maximum lateral force for the resist pattern collapse and the kinetic frictional force for resist sliding on the size of the resist pattern area. (a) resist patterns on the Cr surface, (b) resist patterns on the quartz surface.

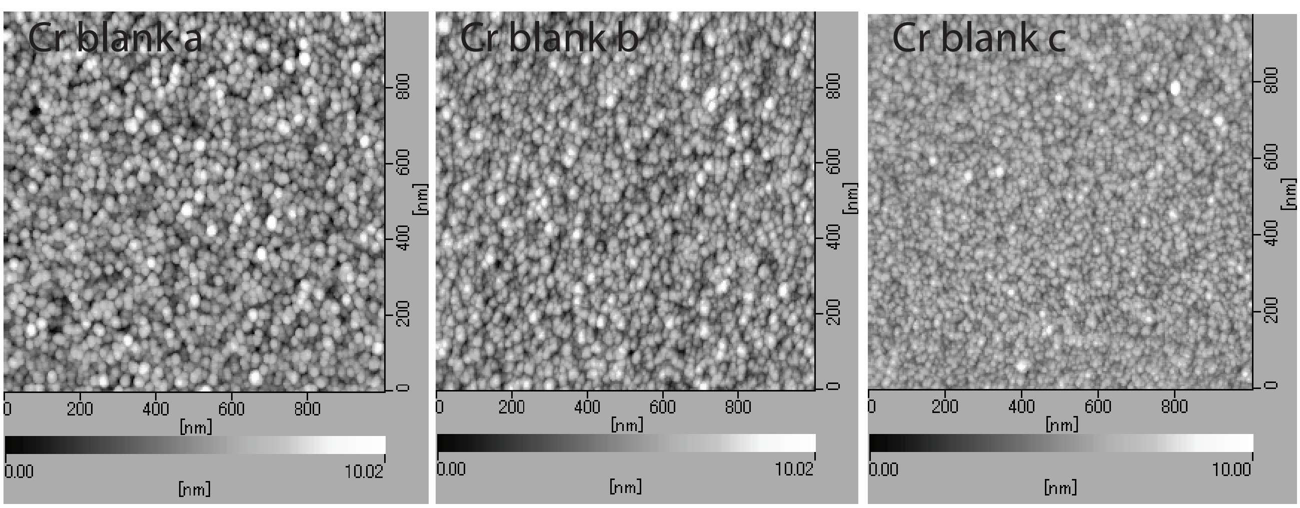

Figure 5. AFM images of three types of Cr blanks a to c.

on the Cr and quartz surfaces, respectively. Both the maximum lateral and the frictional forces changed linearly with the size of the patterned area of the resist/Cr or resist/quartz interface. According to Amontons' law, the frictional force is proportional to the normal load, but is independent of the apparent area of contact. However, in our experiments, as the mass of the used resist patterns was negligible small, there was no contribution of gravitation to the normal load. Rather, the normal load was determined only by the surface force attributable to molecular interactions between the resist and the mask blank surface. Therefore, the normal load was proportional to the patterned area in the absence of external load, and the frictional forces changed linearly as the patterned area increased.[4] The resist patterns on the Cr surface exhibited slightly stronger maximum lateral and kinetic frictional forces than those on the quartz surface. The reason for this difference has not yet been clarified. It is, however, most likely that difference in surface chemical properties and surface roughness between the substrates caused to the different forces.

3.2 Effect of surface roughness for resist adhesion on photomask blank

We examined the effect of the surface roughness of photomask blank. Three Cr blanks with the different surface roughness were prepared. Figure 5 and 6 show AFM images and surface roughness of the Cr blank surfaces.

Cr blank surface C had smallest surface roughness among the evaluated blanks. After n-CAR pattern was formed on each Cr blanks, lateral forces for resist peeling were measured by DP method. Figure 7 shows comparison of resist adhesion of N-CAR on three Cr blanks. As the surface roughness became smaller, resist adhesion also decreases. This suggests that total contacts area between resist and Cr layer is effective factor of the adhesion enhancement. We confirmed that resist

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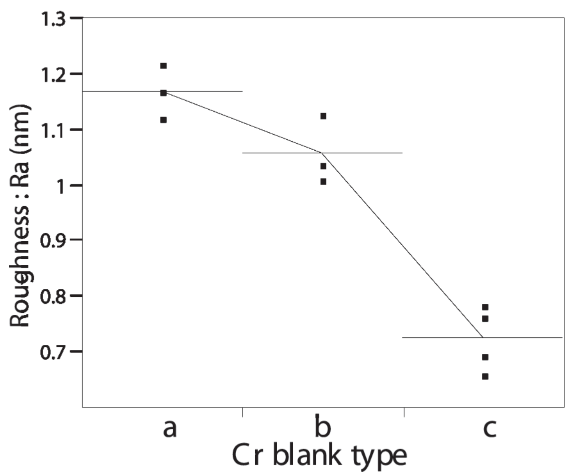

Figure 6. Surface roughness of Cr blank surfaces.

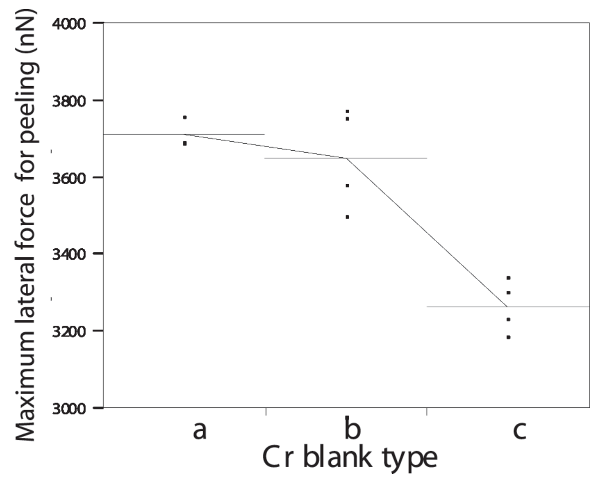

Figure 7. Dependence of maximum lateral force for the resist peeling on the surface roughness of the Cr blanks.

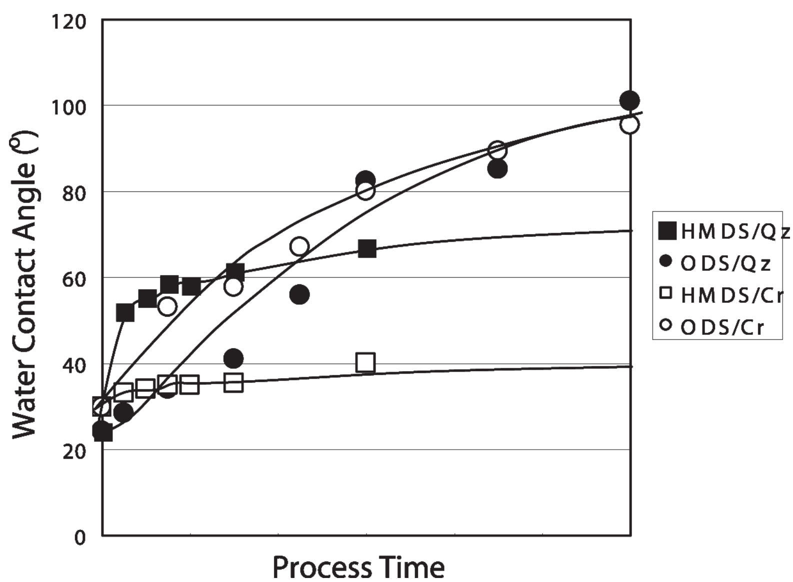

Figure 8. Water contact angles of Cr and quartz surfaces modified by HMDS and ODS as a function of process time.

adhesion on Cr blanks is related to surface roughness with DP method.

3.3 Control of surface energy on photomask blank and adhesion of resist patterns

It has been reported that in order to prevent the resist pattern from being collapsed during the development process, decreasing the surface tension of the rinse or decreasing the aspect ratio of the resist pattern is effective.[5] However, in this study, we focused on preventing resist pattern collapse by enhancing resist adhesion on photomask blank surfaces.

Therefore, we studied the effect of HMDS, which is well known as a resist adhesion promoter in Si processes, on the maximum lateral force in the DP method. To clarify the mechanism of the adhesion enhancement, a similar silanization reagent to HMDS but with a long alkyl chain, ODS, was also investigated as a candidate adhesion promoter. Figure 8 shows water contact angles of Cr and quartz surfaces modified by HMDS and ODS as a function of process time.

Initially, the Cr and quartz surfaces became hydrophilic as a result of the cleaning process. Both surfaces processed by ODS became hydrophobic, and their contact angles reached approximately 100° within 120 min. The contact angles of quartz surfaces covered with HMDS reached approximately 60° within 30 min, while those of the Cr surfaces reached approximately 35° within 30 min during the HMDS treatment.

Figure 9 shows the dependence of resist adhesion measured by the DP method on surfaces with or without HMDS and ODS. The highest adhesion was observed on the quartz surface with HMDS. The adhesion on the Cr surface was not changed by the presence or absence of HMDS, because the Cr surface was

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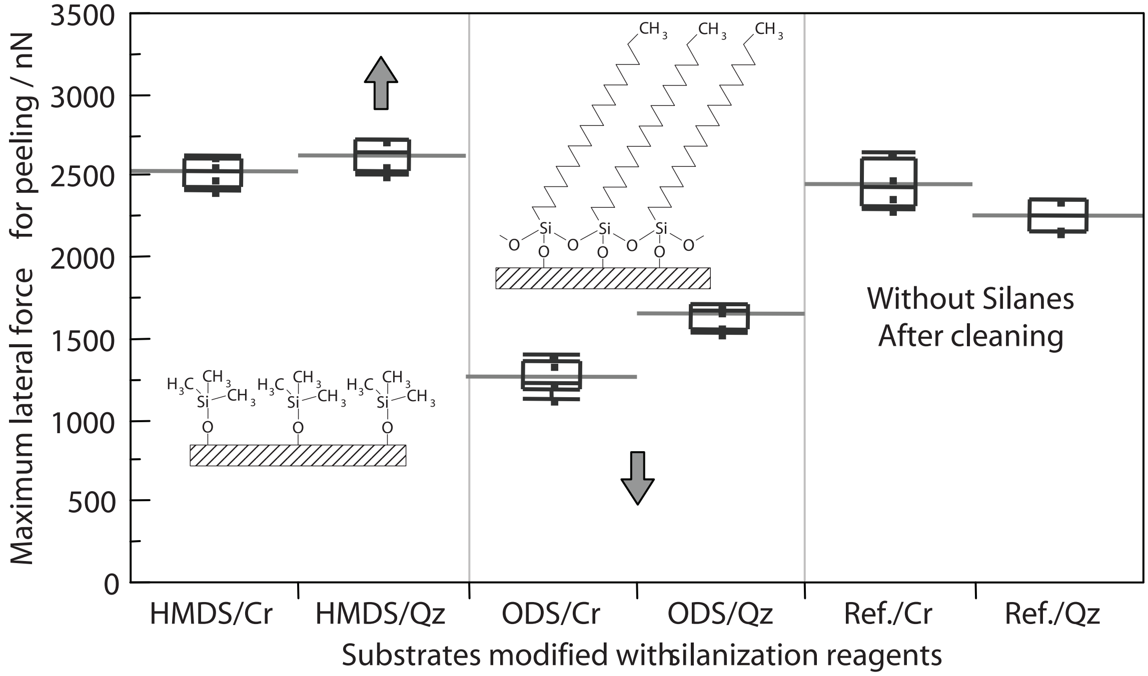

Figure 9. Dependence of resist adhesion measured by the DP method on surfaces modified with or without HMDS and ODS.

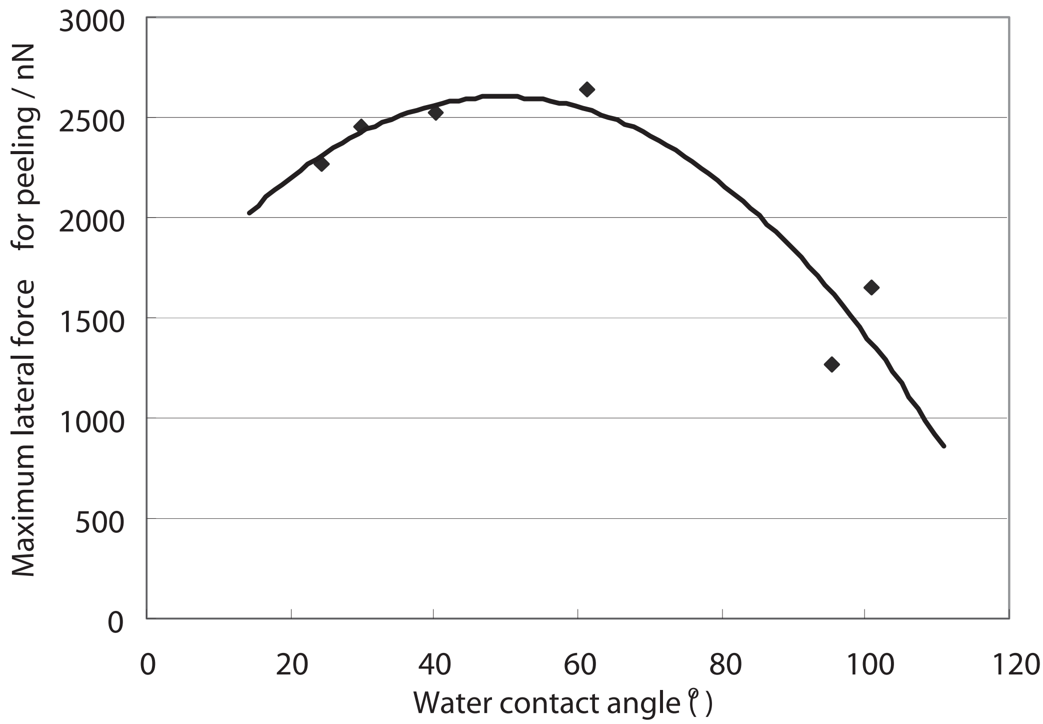

Figure 10. Dependence of maximum lateral force for peeling on water contact angle.

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not fully modified with HMDS, as shown by the lower contact angle on the Cr surface in comparison with that on the quartz surface in Fig. 8. ODS also did not improve resist adhesion. The surface modified with ODS, which was more hydrophobic than that modified with HMDS did not improve the adhesion of resist patterns.

Figure 10 shows dependency of resist adhesion on water contact angles. More hydrophilic and hydrophobic surface did not improve resist adhesion in this n-CAR. Blank surface with water contact angle around 50 degree had largest adhesion in this resist. In order to enhance resist adhesion, it will be necessary to study not only the contribution of van der Waals interactions such as the alkyl-resist interaction but also the contributions of polar, chemical, and ionic interactions at amino- or epoxy-resist interfaces in order to improve adhesion between resist patterns and photomask blanks.

4. Conclusions

Quantitative measurements of resist pattern adhesion on photomask blanks were realized with the DP method. Frictional force of resist patterns on Cr and quartz surfaces was obtained by measuring the maximum lateral forces during the sliding of the collapsed resist pillar. The frictional measurements can be used to analyze not only the physical properties of resist materials but also in, for example, the process of releasing quartz imprint masks from imprinted resists in nanoimprint lithography. Larger contact area between resist and Cr layer is effective for the adhesion enhancement.

Surface energy could be controlled using silanization reagents on the Cr and quartz surfaces. Resist adhesion could be controlled by surface modification using silanes. The combination of silanization with HMDS and a quartz substrate yields the best adhesion among the evaluated substrates. A hydrophobic surface silanized with ODS did not improve the adhesion of resist patterns. The DP method is shown to be effective for measuring the adhesion of micropatterns to photomasks. This method is expected to contribute to the development of microfabrication in next-generation photomasks.

5. Acknowledgment

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6. References

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Industry Briefs

The Semiconductor Photomask Market: to $2.7 Billion in 2011

By **Chiaki Sadanaga,** Communications Manager

The worldwide semiconductor photomask market is estimated to be $2.9 billion in 2008 and forecasted to fall to $2.5 billion in 2009, according to a new market research report available at Electronics.ca Publications.

The electronics industry market research and knowledge network, announces the availability of a new report entitled “Photomask Characterization Summary”.

The worldwide semiconductor photomask market is estimated to be $2.9 billion in 2008 and forecasted to fall to $2.5 billion in 2009, according to a new market research report available at Electronics.ca Publications. Coming out of the current downturn, the photomask market is forecasted to be $2.7 billion by 2011, with advanced technology feature sizes (less than 65 nm) and regions in Asia-Pacific leading the market.

Optical lithography continues to push out new technology approaches, including extreme ultraviolet (EUV), maskless lithography and nano-imprint. Immersion lithography is the technology of choice for 45 nm processing and began high-volume manufacturing in the second half of 2008 - a year delayed from initial announcements. Double-patterning will act as a bridge to 32 nm. Computational lithography has emerged as a promising candidate to extend optical lithography to 22 nm. When and if EUV is adopted will be determined by cost and developing a new supply chain for this revolutionary technology.

This raises perhaps the most daunting challenge faced by photomask suppliers: economic questions outweigh technical issues. As lines shrink, more advanced photomask tools and materials will be required, but due to limited customers migrating to smaller geometries, the photomask industry must balance a shrinking market with escalating development and capital costs.

Rising mask costs are regularly raised as a critical issue in the semiconductor industry, especially for the low-volume-per-design business segments in foundries and ASICs. With lithography parameters approaching their limits and the necessity for continuous improvement, the industry is seeing increasing dialogue and compromises between the technology and design communities.

The new report, Photomask Characterization Summary, provides details on the 2008 Photomask Market for seven regions of world including North America, Japan, Europe, Taiwan, Korea, China, and Rest of World. The report also includes data for each of these regions from 2004 to 2011.

Details of the new report, table of contents and ordering information can be found on Electronics.ca Publications’ web site. View the report: http://www.electronics.ca/publications/products/Photomas ...

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Founded in 1980 by a group of chrome blank users wanting a single voice to interact with suppliers, BACUS has grown to become the largest and most widely known forum for the exchange of technical information of interest to photomask and reticle makers. BACUS joined SPIE in January of 1991 to expand the exchange of information with mask makers around the world.

The group sponsors an informative monthly meeting and newsletter, BACUS News. The BACUS annual Photomask Technology Symposium covers photomask technology, photomask processes, lithography, materials and resists, phase shift masks, inspection and repair, metrology, and quality and manufacturing management.

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Calendar

2009

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spie.org/pm

SPIE Lithography Asia - Taiwan

18-20 November
Sheraton Taipei Hotel
Taipei, Taiwan
spie.org/la

2010

SPIE Advanced Lithography

21-26 February
San Jose Marriott and
San Jose Convention Center
San Jose, California, USA
spie.org/al

Abstracts due 10 August 2009

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